

PATENT SPECIFICATION

790,672



Date of Application and filing Complete Specification March 28, 1956.

No. 9661/56.

Complete Specification Published Feb. 12, 1958.

Index at Acceptance:—Classes 1(2), E2A2; 8(2), D3C; 22, J(1: 5: 9: 10: 12: 19: 33); 46, D3A; and 87(2), A1R58.

International Classification:—B01d. B29d. C04b.

COMPLETE SPECIFICATION

Process of making Recrystallized Silicon Carbide Articles

We, NORTON GRINDING WHEEL COMPANY LIMITED, of Welwyn Garden City in the County of Hereford, a Company registered under the Laws of Great Britain do hereby declare the invention, which was communicated to us by Norton Company, a Company organised and existing under the Laws of the State of Massachusetts, United States of America, of Worcester 6, Massachusetts, United States of America, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

15 The invention relates to the production of recrystallized silicon carbide articles. One object of the invention is to provide a process for making articles of various shapes which consist virtually 100% of silicon carbide crystals integrally united, it being understood that the crystals themselves may have the usual impurities associated with silicon carbide so that they may have as much as 5% impurities by weight but nevertheless cannot be melted and will not dissociate under about 2450° C., their resistance to oxidation being the same as that of the particles of which they are formed; such crystals will for a long time resist oxidation by atmospheric air under 30" barometric pressure at 1400° C. and for a short time at even 1700° C.

Another object of the invention is to make crucibles, vessels, combustion boats, dishes, mortars and laboratory ware of all kinds, which are essentially silicon carbide, i.e. have no bond, by a readily practised process. Another object is to provide a practical process for the manufacture of essentially silicon carbide articles of irregular shapes such as turbine blades, rocket nozzles, venturi tubes and the like.

Another object of the invention is to make strong, refractory filter tubes and filter plates for hydrofluoric acid, both liquid and gaseous.

45 Another object of the invention is to make

superior electrical resistors for heating purposes, as for use in high temperature furnaces.

As conducive to a clearer understanding of the present invention, it is pointed out that silicon carbide cannot be melted at atmospheric pressure. Instead, when heated to about 2250° C., it either sublimes or dissociates (there seems to be some difference of opinion.) Perhaps in some atmospheres it sublimes and in others dissociates or perhaps it first sublimes and later dissociates, but the important point is that at the critical temperature it changes directly from solid into gas. Therefore silicon carbide cannot be melted and cast and it cannot be sintered, since sintering, as the term is now understood, depends upon the possibility of a liquid phase at the pressure involved. Sintering can usually be done at temperatures far below the melting point.

It is known that silicon carbide can be recrystallized. In this phenomenon, the crystals of silicon carbide when closely packed together (but not necessarily under mechanical pressure) grow together when heated to about the temperature of formation of silicon carbide (about 2000° C.) or at temperatures slightly higher. This phenomenon is not dependent upon the possibility of a liquid phase at the gaseous pressure involved. We may here point out that the provision of gaseous pressure of much above atmospheric at temperatures of 2000° C. and above presents great practical difficulties.

Whether or not sintering (later developed) may not, after all, be in some cases scientifically somewhat the same as recrystallizing, we are not prepared to say. However, as a practical matter the recrystallizing process, known commercially substantially only in connection with silicon carbide, has heretofore been limited to the production of simple shapes, such as round rods, and chiefly used for the manufacture of electrical resistor rods of silicon carbide. In the manufacture of

50

55

60

65

70

75

80

85

90

such rods, silicon carbide crystals, mixed with a non-contaminating temporary binder such as sodium silicate solution, has been tamped into steel tubes; later the tamped rods were removed and fired. But this procedure is not satisfactory for making more difficult shapes such as those mentioned and others such as hollow rods.

For the manufacture of shapes other than very simple ones such as solid cylinders, the slip casting technique has been one of the most practical in the ceramic and allied arts. However, the heretofore usually produced sizes of silicon carbide could not be successfully slip cast and recrystallized. We believe that no one else has prior to our invention produced, by the true slip casting technique, silicon carbide articles of practically 100% silicon carbide crystals, the articles being uncracked and of sufficient strength.

We have now discovered how to make integral silicon carbide articles by slip casting and firing. We use no permanent bond, so that the articles are as refractory as the silicon carbide itself. If we use green silicon carbide or light grey silicon carbide (higher than 99% pure) our articles will stand temperatures up to 2400° C. in reducing atmospheres.

EXAMPLE I

We made up a slip of 37.5% water and 62.5% silicon carbide (by weight, of course). We then added .5% of a wetting out agent, which itself was mostly water but had in solution about 25% of sodium dioctylsulpho-succinate. The silicon carbide was 30% 100 mesh up to 325 mesh and 70% very fine, meaning 5 microns and finer. It was the green variety, higher than 99% pure SiC. We mixed the foregoing thoroughly, then poured the resulting slip into a plaster of Paris mould, added more slip from time to time until the desired thickness was attained, then decanted the supernatant slip, dried for ten minutes in the mould, took the mould apart, dried the article further at about 100° C. for one day, and then fired the article for ten minutes in a reducing atmosphere at 2250° C. The furnace for firing was an electric resistor tube furnace but other furnaces could be used. Also any other wetting out agent, of which there are many, could be used. Examples are the alkaline sulphonated alcohols, the alkaline alkyl sulphates, and the alkaline sulphonated aromatics.

EXAMPLE II

The procedure, the ingredients and the proportions were exactly the same as in Example I excepting that the silicon carbide was 40% 100 mesh on to 325 mesh and 60% very fine, meaning 5 microns and finer.

The articles made first according to Examples I and II were crucibles for laboratory use. However, any other shape of article can be similarly made, merely the mould is

varied. For making nozzles and venturi tubes, we used four piece moulds and kept on pouring slip until the walls were solid. The same technique can be used for making turbine blades, namely to use a multipart mould and to keep on pouring until the piece is solid.

In all cases the porous mould, usually of plaster of Paris, removes water and all but less than 1% of material other than silicon carbide crystals. Porous moulds of material other than plaster of Paris could be used.

EXAMPLE III

The procedure, the ingredients and the proportions were exactly the same as in Example II (in which there was 37.5% water and 62.5% silicon carbide) excepting that in Example III we provided 20% water and 80% silicon carbide and we provided in place of the formerly mentioned wetting out agent, 0.83% on the water content of diluted (50% water solution) sodium silicate as a deflocculant. This is an electrolyte and functions as such, keeping the particles in suspension. It acts as a dispersing agent. During the firing any residue of sodium silicate is dissociated, the sodium passes off as vapour, the oxygen unites with the reducing atmosphere, and the silicon forms more silicon carbide uniting with the carbonaceous vapour present. The tube of the furnace employed was a graphite tube.

All articles were smooth (the articles of Example III was a crucible too) and each had a porosity of about 30% but each would hold water. Crucibles made as described can be used in which to melt various refractory metals and compounds. They do not leak, spall, crack, craze nor melt nor vapourize at temperatures below about 2450° C. They can be used in air up to 1400° C. or for a short time at up to 1700° C.

The slip employed should be at least 10% water, and have at least 4.5% silicon carbide crystals, the silicon carbide being at least 50% fines no larger than 40 microns. If articles of no greater than 30% porosity are wanted, the slip should have at least 20% particles between 80 mesh size and 325 mesh size. The silicon carbide should be, on the average, at least 95% pure. The firing should be done in a reducing atmosphere (it was an atmosphere of C^o) or in a silica or silicon vapour atmosphere, at a temperature between 2100° C. and 2400° C. We believe that the reason for success in slip casting and recrystallizing silicon carbide articles is in the use of fines which are of colloidal size, and that colloidal size silicon carbide fines have properties very much the same as clay. Apparently no one appreciated this before. The wetting out agents and deflocculant can be generically referred to as dispersing agents. The proportions given for the slip are by weight.

The porosity of the articles made in accord-

ance with the present process can be controlled by varying the parameters of the recrystallizing technique and also by varying the particle sizes. More complete recrystallizing is achieved either by raising the temperature for the recrystallizing steps of the process or by increasing the time at a given temperature, or by firing in an atmosphere such as silica vapour, or by all three. Strangely, a more completely recrystallized article has pores which are more anastomosing than one which is less completely crystallized. On the other hand the finer (smaller) the sizes of the particles, or the greater the proportion of finer particles, the less will the pores interconnect. For liquid tight articles from 30% to 55% of the particles between 80 and 325 should be used. A slip of *all* fines will produce porous pieces but for some uses such as filter tubes and filter plates these are very useful.

In the examples the particles of the different sizes were thoroughly mixed before adding the water in a rotating container having rubber balls. Any other means of thorough mixing could be used, and mixing can be done after the water and dispersing agent are added. Drying can be done in the mould if desirable as in the case of very complicated pieces, but it is frequently simpler to do most of the drying outside of the mould. The articles could even be fired in the moulds but that would destroy the moulds.

Proceeding according to Example III, we made some crucibles which thereafter were used for melting synthetic mica with very practical results, as the mica after resolidification was uncontaminated and none of it penetrated into or leaked through the crucibles.

EXAMPLE IV

The procedure, the ingredients and the proportions were exactly the same as in Example III excepting that we fired the crucibles at 2400° C. for one half hour. These crucibles had anastomosing (interconnecting) pores and were permeable to water, and also most molten metals. Tubes or plates so made are useful for filtering hydrofluoric acid, liquid or gaseous, and other highly corrosive liquids and gases which attack porcelains but will not attack silicon carbide.

The articles made according to Example I are not permeable to water and most molten metals. Articles made in accordance with Example II are permeable to water in about half an hour but are impermeable to most molten metals. Articles according to Example III get damp on the outside when filled with water but do not pass it readily and will hold most molten metals except silicon.

In the recrystallizing step of the process, the fine, medium and large crystals start to grow together as soon as the critical temperature is reached. The higher the temperature, the

faster the growth and the longer the time at temperatures of recrystallization, the greater the growth. At first the pores are small, like the crystals, and are not highly anastomosing, that is they do not freely interconnect. But as the crystals grow, the pores become more and more interconnected and the articles become more and more permeable. However it is not represented that the total porosity (volume of pore space) is much if any greater in Example IV than it is in Example I. In fact our estimate is that the total porosity was about the same for all Examples I, II, III, IV, and V.

EXAMPLE V

We made up a slip of 15.2% water and 84.8% silicon carbide, by weight. The silicon carbide was 50% 100 mesh on to 325 mesh and 50% very fine, meaning five microns and finer. It was the green variety, higher than 99% pure SiC. To this we added 1% of the wetting out agent of Example I, and .2% of sodium silicate of Example III as a deflocculant. The wetting agent is not necessary in this case, however, it is used to speed up the wetting. These percentages are percentages on the water and silicon carbide previously mentioned.

The slip ingredients were thoroughly mixed and then poured into a plaster of Paris mould to produce a rocket nozzle of venturi shape. This was a hollow relatively thin walled rocket nozzle shape weighing, when finished, about four and a half pounds. The mould was all of plaster of Paris made in four parts to leave, when joined, a cavity of the hollow paraboloidal or hyperboloidal shape of the venturi tube desired, with a sprue hole through which to pour the slip. The mould was placed so that the axis of the venturi was horizontal with the sprue hole axis vertical.

After pouring the slip to fill the cavity and the sprue hole to the very top, it was only about half an hour until most of the water had been absorbed by the plaster of Paris leaving the silicon carbide filling the space in the mould. However, while the water was being absorbed more slip was added from time to time to keep the level up to the top of the sprue hole as naturally the level would lower as the water was absorbed. It is desirable in slip casting to maintain the most hydraulic pressure available that is by keeping the sprue hole full to the top.

The signal to open up a mould of this kind is when no more slip can be added to the sprue hole, that is to say when settling has ceased. Thereupon we took the mould apart and gently handling the nozzle we set it in a chamber and dried it at 150° F. for 12 hours.

This venturi nozzle was then recrystallized at a temperature of about 2450° C. in a graphite chamber above a graphite crucible containing silica sand, with a baffle between them. The article was therefore fired in an atmos-

phere of silica vapour which was also to some extent a reducing atmosphere on account of the hot graphite. This technique is fully described in our British Patent Specification No. 716,083, it being understood that our venturi nozzle of silicon carbide was substituted for the graphite nozzles shown and described in the above patent.

The silicon carbide grain of which this nozzle was made was well recrystallized and formed an integral shape. By reason of the atmosphere of silica vapour during the recrystallizing a silicon carbide structure was formed which consisted of crystals of SiC at least 10 times as large as those formed in recrystallizing as described in previous examples. Nevertheless the surface of the rocket nozzle was very smooth to the touch. Shapes with large crystals of this type are more resistant to flame and their surfaces are harder than those of smaller crystal size. The crystals in size were about the size of the 100 mesh silicon carbide that was used. From this the order of size of the crystals in the other examples can readily be understood.

It should be understood that the recrystallizing in an atmosphere of silica vapour is a step which can be used in all variations of the invention. That is to say the ingredients and proportions of any of the previous examples can be used to make shapes which are fired to recrystallize in an atmosphere of silica vapour.

At the end of the firing which takes about three hours, of which about one hour is at the firing temperature mentioned, the graphite crucible originally filled full of silica sand contained nothing but silicon by reason of which it appears that during the latter part of the firing at least the atmosphere was silicon vapour instead of silica vapour. The oxygen is, of course, gradually removed from the silica by the hot graphite which accounts for the change. Therefore it clearly appears that the superior results of firing in an atmosphere of silica vapour can also be obtained at least to a large degree by firing in an atmosphere of silicon vapour.

For many purposes, such as for crucibles for melting materials such as synthetic mica which must be protected from contamination, the articles should be substantially all silicon carbide crystals. But for other purposes one or more other refractory hard carbides can be mixed with silicon carbide to make the slip. The refractory hard carbides are TiC, VC, CrC, ZrC, HfC, NbC, MoC, TaC, WC and B₄C. All of these carbides are refractory above 2000° C. and outside of radioactive materials we believe this is a complete list of the hard refractory carbides. Two or more of them can be used in combination with the silicon carbide, but in all cases there should be at least 50% silicon carbide present in the total solid insoluble mineral constituent.

We have explained that sometimes it is desirable to use a wetting agent, a deflocculating agent, a dispersing agent or an electrolyte. Many of these are organic, but some are inorganic (as the alkali or alkaline earth salts of the halogens) and soluble in water. Thus normally the sole solid insoluble mineral constituent will be hard refractory carbide crystals. However, we have found we can use a minor portion, up to 10%, of certain hard refractory oxides such as alumina and zirconia. These in the recrystallizing step become carbides at least in part because of the reducing atmosphere. Adding small percentages of the oxides to the carbides is deemed to be included in the process of this invention.

As our invention is a process we should not be required to be more specific than in the following claims since any material might be added to the slip so long as the slip will cast in a porous mould, which is preferably plaster of Paris, and so long as the mould will remove enough of the water to coalesce the crystals to form an article which can be handled without breaking, because if the added material is organic it will disappear in the firing, if the added material has a vapour phase below 2100° C. it will also disappear in the firing and if the entire mixture will recrystallize the article can be made by the process of this invention.

What we claim is:—

1. The process of making recrystallized silicon carbide articles comprising preparing a free flowing slip of water and silicon carbide crystals, said slip having at least 10% water and having at least 45% silicon carbide crystals which are at least 50% fines no larger than 40 microns and which are at least 95% pure SiC, casting the slip in a porous mould and by means of said porous mould removing sufficient of the water to coalesce the crystals to form an article which can be handled without breaking, drying the article and then firing it and recrystallizing it in a reducing atmosphere at between 2100° C. and 2450° C., all percentages being by weight.

2. Process according to Claim 1 in which the atmosphere is also a silica vapour atmosphere.

3. Process according to Claim 1 in which the atmosphere is also a silicon vapour atmosphere.

4. The process as claimed in any of the preceding claims wherein at least 50% of the solid insoluble mineral component of said slip is silicon carbide crystals.

5. The process as claimed in any of the preceding claims wherein the silicon carbide employed has added thereto any of the following carbides or a mixture of such carbides, namely TiC, VC, CrC, ZrC, HfC, NbC, MoC, TaC, WC, or B₄C.

6. The process as claimed in any of the preceding claims wherein up to 10% of refrac-

70

75

80

85

90

95

100

105

110

115

120

125

130

tory oxides are added to the silicon carbide.

7. The process of making silicon carbide articles substantially as described.

8. Articles of silicon carbide made by the process claimed in Claim 7.

9. Articles of silicon carbide made in accordance with the foregoing examples.

MARKS & CLERK.

Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press,—1958.
Published at the Patent Office, 25, Southampton Buildings, London, W.C.2, from which
copies may be obtained.

REST AVAILABLE COPY